P 25/4

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Project Summary

Development of Methods and Analysis of Particulate Sampler Data from RAPS

Sandor J. Freedman and William M. Yeager

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Methods were formulated, tested and demonstrated to statistically analyze and graphically process analytical data derived from dichotomous particulate samplers operating at ten Regional Air Monitoring System (RAMS) stations in the greater St. Louis area.

Statistical techniques and computer programs are documented in this report and the sample outputs are presented for the following tasks:

- **Time series plots of total mass and sulfate 24-hr averages for high volume and dichotomous sampler instruments**
- **Means and standard deviations of total mass and sulfate by station by quarter for high volume and dichotomous samplers**
- **Correlations between high volume and dichotomous sampler measurements of total mass and sulfate at each station**
- **Scatterplots of high volume vs. dichotomous sampler measurements for total mass and sulfate at each station**
- **Frequency distributions for the fine/total ratio of total mass, sulfate, and lead at each station for dichotomous sampler measurements**
- **Correlations between the fine and coarse fractions for 23 elements plus total mass at each station for dichotomous sampler measurements**
- **Correlations among six selected elements and total mass at each station by fraction for dichotomous sampler measurements**

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This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A recently developed technique, using the dichotomous sampler coupled with X-ray fluorescence analysis of samples, has facilitated the determination of the mass and elemental in concentrations for particulate matter collected from ambient air in two different size ranges. The data consist of measurements taken in the years 1975, 1976, and 1977 at ten sites in the greater St. Louis area. Continuous sampling was conducted, and periods between filter changes ranged from 2 to 12 hours. The sites coincided with 10 of the 25 sites of the Regional Air Monitoring System (RAMS), a part of the Regional Air Pollution Study (RAPS). Site locations

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EP 1. 89/2:

ranged from urban to rural areas at varying distances from a variety of industrial point sources as well as sources of emissions from mobile vehicles. Data generated by the RAMS monitoring program include particulate mass and sulfate from a standard hi-volume sampler as well as a variety of measurements of other atmospheric conditions.

The data provide a unique opportunity for investigating relationships between air quality and emissions as well as the spatial and temporal characteristics of ambient pollutant concentrations. The work reported herein consists of the development and implementation of computer-assisted methodology for presentation and analysis of dichotomous particulate sampler data. The analyses include the following:

- Time series plots, scatter plots, and correlations of 24-hour averages of total mass and sulfate for high volume and dichotomous sampler data at each station
- Means and standard deviations of total mass and sulfate by station by quarter for high volume and dichotomous samplers
- Frequency distributions for the fine/total ratio of total mass, sulfate, and lead at each station for dichotomous sampler measurements
- Correlations between the fine and coarse fractions for 23 elements and total mass at each station for dichotomous sampler measurements

Monitoring

The RAMS network consisted of 25 stations strategically located throughout the greater St. Louis area. Dichotomous samplers and hi-volume samplers were operated at ten of the sites (See Table 1). These sites lay along four concentric circles centered in downtown St. Louis with radii of 4, 10, 20 and 40 kilometers, respectively. The sites represented a diverse range of sampling environments from heavily trafficked, inner city areas to industrial locations to agricultural settings. Choice of site locations was based primarily upon the extent of surrounding pollutant emission sources (stationary or mobile) and the significance of topographical features capable of influencing local air flow.

The automated dichotomous sampler operates on the principle of virtual impaction. That is, particles are impacted into a slowly pumped void thus eliminating the problem of particle bounce on collection surfaces. The device collected particles in two size ranges: fine ($<2.4\,\mu m$) and coarse (2.4 to 20 μm). Filters from the dichotomous sampler were sent to Lawrence Berkeley Laboratory (LBL), Berkeley, CA for mass and elemental analysis.

X-ray fluorescence spectroscopy was employed at LBL to determine the elemental composition of samples in both fine and coarse fractions. The composition of a sample was determined by irradiation with a beam of X-ray and observation of the emissions of characteristic K and L X-rays. The procedure was well suited for analysis of elements heavier than Mg in atomic weight. The following elements were analyzed: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Cd, Sn, Sb, Ba, and Pb. A beta gauge was used to determine total mass for both fine and coarse fraction samples. The beta gauge method for aerosol mass determination had an accuracy of 12 $\mu g/m^3$ for 2-hr samples and 2 $\mu g/m^3$ for 12-hr samples. The reproducibility of the X-ray fluorescence measurements was found to be within 5% for major elements.

Hi-volume particulate samplers were also operated at each of the 10 dichotomous sampler sites in the RAMS network. Samples were collected for 24-hour periods every third day. Hi-volume samples were analyzed by Rockwell International for total particulate mass, sulfate and nitrate concentrations. Dichotomous samplers and hi-volume samplers were operated simultaneously side-by-side; pollutant data collected simultaneously were matched for comparison of the two types of instruments.

Results

Tables 1 and 2 show comparisons of the high volume and dichotomous sampler results. For both total mass and sulfate, the high volume instrument collects significantly greater amounts than does the dichotomous sampler. Overall, the ratio of high volume and dichotomous sampler results is 1.87 ± .03 for total mass, 1.47 ± .02 for sulfate. There are no significant differences between stations in the ratios for either mass or sulfate. The central sites have the largest concentration of both mass and sulfate. In general, the mass concentrations were highest during the second quarter (April-June); the sulfate concentrations were highest during the third (July-September). For total mass the overall correlation coefficient is 0.671, varying from 0.377 at station 120 to 0.860 at

Table 1. Linear Regression Analysis Hi-Volume Mass vs. Dichotomous Total Mass

Station Number	No. of Cases	Mean HV/DS Ratio	S.D. HV/DS Ratio	Corr. Coeff.	Intercept[a] ($\mu g/m^3$)	95% Conf. Interval	Slope[b]	95% Conf. Interval
103	120	1.93	0.85	0.637	43.99	-16.28→104.26	0.902	0.703→1.101
105	118	2.04	0.78	0.646	49.46	+ 0.24→ 98.68	0.786	0.615→0.957
106	95	1.76	0.82	0.666	29.40	-20.88→ 79.68	0.967	0.744→1.190
108	91	1.96	1.09	0.708	31.50	-24.23→ 87.23	1.051	0.830→1.272
112	115	1.73	0.71	0.722	21.11	-37.26→ 79.48	1.143	0.938→1.348
115	111	1.57	0.52	0.860	14.33	-12.56→ 41.22	1.074	0.953→1.195
118	104	2.18	1.33	0.514	37.02	-15.01→ 89.05	0.809	0.544→1.074
120	97	1.71	1.09	0.377	31.06	-28.80→ 90.92	0.682	0.340→1.024
122	112	1.72	0.92	0.594	22.27	-26.49→ 71.03	0.861	0.640→1.082
124	77	2.17	1.32	0.433	28.33	-23.56→ 80.22	0.919	0.478→1.360
All	1040	1.869	0.970	0.671	27.04	-25.81→ 79.89	1.020	0.951→1.089

[a] *The intercept of the regression line is the predicted value of the HIVOL mass when the dichotomous sampler mass is zero.*
[b] *The slope of the regression line is the predicted change in HIVOL mass for unit change in dichotomous sampler mass.*

Table 2. Linear Regression Analysis Hi-Volume Sulfate vs. Dichotomous Sulfate

Station Number	No. of Cases	Mean HV/DS Ratio	S.D. HV/DS Ratio	Corr. Coeff.	Intercept[a] ($\mu g/m^3$)	95% Conf. Interval	Slope[b]	95% Conf. Interval
103	132	1.47	0.65	0.857	4.574	-1.893–11.041	0.791	0.708–0.874
105	141	1.39	0.34	0.964	2.815	-0.796– 6.426	0.939	0.896–0.982
106	103	1.35	0.45	0.937	2.983	-3.435– 9.401	0.916	0.848–0.984
108	105	1.47	0.66	0.811	4.647	-3.990–13.284	0.778	0.668–0.888
112	143	1.39	0.83	0.818	2.927	-6.576–12.430	0.928	0.819–1.037
115	129	1.35	0.46	0.904	3.418	-1.979– 8.815	0.808	0.741–0.875
118	110	1.53	0.75	0.854	4.725	-1.870–11.320	0.706	0.624–0.788
120	106	1.80	1.35	0.637	3.705	-9.418–16.828	0.949	0.725–1.173
122	121	1.53	0.66	0.702	3.711	-8.715–16.137	0.888	0.724–1.052
124	78	1.45	0.55	0.952	2.695	-2.932– 8.322	0.951	0.881–1.021
All	1168	1.47	0.72	0.838	3.620	-4.481–11.721	0.864	0.832–0.896

[a]*The intercept of the regression line is the predicted value of the HIVOL mass when the dichotomous sampler mass is zero.*
[b]*The slope of the regression line is the predicted change in HIVOL mass for unit change in dichotomous sampler mass.*

station 115. The correlation coefficients for sulfate are higher, with an overall value of 0.838, varying from 0.637 at station 120 to 0.964 at station 105.

Differences between the measurements by high volume and dichotomous samplers may be at least partially explained by differences in the design of the two instruments. The high volume sampler had essentially no upper cutoff for particle size, but the dichotomous sampler rejected particles with diameters greater than 20 μm. Although particle size distributions were not measured by the RAMS instruments, previous studies have shown that aerosol particles have a bimodal size distribution, with different sources for each mode. The fine particle mode (< 2 μm in diameter) is primarily due to combustion products. The coarse particle mode (> 3 μm in diameter) results from dispersion of mechanically generated particles, especially soil. The greater total mass measured by the high volume samplers may be due to particles larger than 20 μm diameter in St. Louis aerosol. Known sources of dust in the area include road dust, rock quarries, cement manufacturing, and wind erosion of soil. Application of a chemical element balance model to the dichotomous sampler data from St. Louis indicated that crustal components account for 43% of the total mass.

Another difference between the high volume and the dichotomous samplers is in the filter media. The former used glass fiber filters while the latter used cellulose ester membrane filters. Glass fiber filters are known to collect artifact SO_4 in the presence of SO_2 gas. This may account for the larger amounts of sulfate collected in the high volume samplers. The higher correlations between the high volume and dichotomous measurements of sulfate probably result from the fact that most of the sulfate (89%) is in the fine fraction, which is not affected by differences in inlet design.

Other differences between the two instruments include the lack of symmetry in the gable roof of the volume sampler, which makes its collection efficiency sensitive to wind direction. The dichotomous sampler used inlets having axial symmetry. The high volume samplers were operated from midnight to midnight on a three or six day cycle; filters remained in the instrument for several hours after the air flow was shut off, which could have allowed some additional particles to have settled onto them.

The analysis of the dichotomous sampler data by size fraction showed that the total mass was approximately equally divided between the fine and the coarse fractions. There was no significant site dependence in the ratios of fine to total mass and elemental concentrations. Overall, the ratio was 0.518 ± .001 for mass, 0.885 ± .001 for sulfur and 0.799 ± .001 for lead. The correlation between fine and coarse fractions was highest for bromine and titanium, lower for lead and sulfur, and even lower for total mass. The correlations among elements were highest for sulfur with total mass in the coarse fraction, for iron with total mass in the fine fraction, and for lead with bromine in both fractions. The high correlation between lead and bromine is expected, since both are due to auto emissions.

Sandor J. Freedman and William M. Yeager are with System Sciences, Inc., Chapel Hill, NC 27514.
***Thomas G. Dzubay** is the EPA Project Officer (see below).*
The complete report, entitled "Development of Methods and Analysis of Particulate Sampler Data from RAPS," (Order No. PB 81-179 327; Cost: $17.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
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The EPA Project Officer can be contacted at:
Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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